

A SURVEY OF DISLODGEABLE
ORGANOPHOSPHATE RESIDUES ON SELECTED CROPS
IN FRESNO AND MERCED COUNTIES
AT THE TIME OF HARVEST DURING FALL OF 1985

By

Keith T. Maddy, Chief/Staff Toxicologist
Clifford R. Smith, Senior Environmental Hazards Scientist
Yvette Brittain, Environmental Hazards Scientist
Dorothy Alcoser, Environmental Hazards Scientist
Jonathan Wanjiru, Environmental Hazards Scientist
Sheila Margetich, Agricultural Chemist

HS-1369 August 20, 1986

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Branch
1220 N Street, Sacramento, California 95814

SUMMARY

During October and November 1985, 57 foliar samples were collected from crops grown in Fresno and Merced counties. Detectable pesticide residues of azinphos-methyl (Guthion^R) and phosmet (Imidan^R) were found on eight of the 57 samples. None of the residues exceeded the established safe levels for any of the pesticides detected.

INTRODUCTION

The Worker Health and Safety Branch of the California Department of Food and Agriculture conducts day of harvest surveys in several different areas of the state throughout the year. These surveys serve to assess the protection provided by worker reentry intervals and monitor pesticide degradation under the different climatic conditions that exist in the state. Hand harvest and/or manual labor intensive crops are selected for these surveys, since they provide the greatest risk of prolonged exposure to foliar pesticide residues.

METHODS

Foliage samples of lettuce, broccoli, and tomatoes were collected from areas of the field where the workers were harvesting the crop. The apple samples were collected from four different areas of the tree and 10-12 trees were sampled on a diagonal line in orchards where harvesters were present. A Birkestrand leaf punch was used to collect 48-50 leaf disks per sample in a glass jar. The leaf punch was cleaned with isopropyl alcohol between samples. The glass jars were sealed with aluminum foil, capped, and shipped on wet ice to the Worker Health and Safety Laboratory in Sacramento for next-day analysis. The analytical method is detailed in Appendix I. Appendix II lists the pesticides screened for in the analysis.

RESULTS

Table I lists the total number of samples and positive samples collected, and the counties and crops surveyed during this study. All of the 57 samples were obtained during October and November 1985. All of the positive samples were collected from apple orchards in Merced county. Table II lists the amount of residues and type of pesticide detected in the positive samples.

DISCUSSION

The estimated safe level of dislodgeable foliar pesticide residues for phosmet (Imidan^R) is 11.30 ug/cm². This value was derived from a ratio proportion calculation detailed in reference 1. Residues of phosmet were detected in three of the positive samples in amounts that were less than one percent of the calculated safe level.

The established safe level of dislodgeable foliar pesticide residues for azinphos-methyl (Guthion^R) is 1.60 ug/cm². Residues of azinphos-methyl were detected in six of the positive samples. The amount of residue detected in four of the samples was less than 53 percent of the safe level. The amount of azinphos-methyl found in the other two samples was near the safe level. None of the residue levels detected exceeded the safe level.

Residues of azinphos-methyl have been detected in amounts near and above the safe level in previous surveys (see references 2 and 3) of Fresno, Sacramento and Yolo counties. Degradation studies conducted in these areas in a variety of orchards may be necessary to assess the current reentry

interval.

CONCLUSION

The data collected during this survey supports data gathered in previous surveys. Future studies are planned to provide additional information necessary to evaluate the adequacy of the reentry interval for azinphos-methyl. The Worker Health and Safety Branch will continue to conduct monitoring of farm fields for pesticide residues.

TABLE I

1985 Fall Dislodgeable Pesticide Residue Survey

<u>Crop</u>	<u>Fresno</u>		<u>Merced</u>	
	<u>Total</u> <u>Number</u>	<u>Number</u> <u>Positive</u>	<u>Total</u> <u>Number</u>	<u>Number</u> <u>Positive</u>
Broccoli	2	0	0	0
Lettuce	41	0	0	0
Tomatoes	5	0	0	0
Apples	0	0	9	8

TABLE II

Dislodgeable Pesticide Residues Detected in Merced

<u>Pesticide</u>	<u>ug/cm²</u>
Azinphos-methyl	1.46
Azinphos-methyl	0.82
Azinphos-methyl	0.84
Azinphos-methyl	1.44
Azinphos-methyl	0.27
*Azinphos-methyl	0.051
*Phosmet	0.050
Phosmet	0.067
Phosmet	0.081

*Both of these residues were detected in one sample.

APPENDIX I

ANALYTICAL PROCEDURES

The Screening of Dislodgeable Pesticide Residues

SCOPE: This method is for the screening of dislodgeable organophosphate pesticide residues on vegetation.

PRINCIPLE: Most organophosphate pesticides are very soluble in ethyl acetate; therefore, this solvent is used to extract the pesticide. The analysis is by gas chromatography with a NP detector.

REAGENTS AND EQUIPMENT:

- (1) Sur-ten
- (2) Ethyl acetate, nanograde
- (3) Sodium sulfate anhydrous
- (4) Rotary evaporator
- (5) Rotator
- (6) Various glassware
- (7) Gas chromatograph with NP detector

ANALYSIS: About 75 ml of water and four drops of 2% Sur-ten are added to the bottle containing the sample. The bottle is rotated for an hour. Decant off the water. This is repeated twice with two drops of Sur-ten and 50 ml water each time. To the combined amount of water in a separatory funnel 75 ml ethyl acetate is added. The funnel is shaken gently for two minutes. The ethyl acetate is allowed to run through 50 g of sodium sulfate anhydrous. The water is extracted two more times with 50 ml of ethyl acetate each time. The combined solvent is evaporated to dryness and redissolved in 5 ml of ethyl acetate. This is ready for organophosphate analysis with the NP detector.

Gas chromatograph condition:

Column: (1) 6 ft. 4% OV-101
(2) 6 ft. 50/50 mixture of 4% OV-101 and 6% OV-210
Oven: 170°C and 230°C
Injector: 250°C
Detector: 350°C
Gas flow: 30 ml/min

CALCULATIONS:

$$\frac{\text{ug}}{\text{sq cm}} = \frac{(\text{ng std}) (\text{peak ht sample}) (\text{final vol ml})}{(\text{peak ht std}) (\text{ul injected}) (\text{total area sq cm})}$$

$$\text{Total area} = (2N) (3.14) (r) (r)$$

Where N = number of disc in sample
r = radius of disc in cm

DISCUSSION: Sensitivity: 0.0001 ug/sq cm in parathion

REFERENCE: Zweig, Vol. VI, p. 132, p. 191.x

APPENDIX II

ORGANOPHOSPHATE SCREEN

Pesticide

Azinphos-methyl (Guthion)	Isofenphos (Oftanol)
Carbophenothion (Trithion)	Malathion
Chlorfenvinphos (Supona)	Methamidophos (Monitor)
Chlorpyrifos (Dursban)	Methidathion (Supracide)
Coumaphos (Co-Ral)	Mevinphos (Phosdrin)
Crotoxyphos (Ciodrin)	Naled (Dibrom)
Demeton (Systox)	Oxydemeton-methyl (Metasystox-R)
DDVP	Parathion-ethyl
Dialifor (Torak)	Parathion-methyl
Diazinon	Phorate (Thimet)
Dicrotophos (Bidrin)	Phosalone (Zolone)
Dimethoate (Cygon)	Phosmet (Imidan)
Dioxathion (Delnav)	Phosphamidon (Dimecron)
Disulfoton (Disyston)	Profenofos (Curacron)
EPN	Propetamphos (Safrotin)
Ethion	Ronnel
Ethoprop (Mocap)	Schradan (OMPA)
Fenamiphos (Nemacur)	Sulprofos (Bolstar)
Fenitrothion (Sumithion)	Tetrachlorvinphos (Gardona)
Fensulfothion (Dasanit)	Thionazin (Zinophos)
Fenthion (Baytex)	Triazophos (Hostathion)
Fonophos (Dyfonate)	

Other Chemicals Also Detected Using a Nitrogen-Phosphorus Detector

Molinate (Ordram)
Thiobencarb (Bolero)

Sensitivity

The Minimum Detectable Level (MDL) for each of these chemicals is at least 0.1 ug/cm² of leaf surface except for azinphos-methyl (Guthion) (2.5 ug/cm²)* and phosalone (Zolone) (1 ug/cm²). A more sensitive MDL may be obtained depending on the specific chemical and sample matrix.

* In this study, a specific analysis was completed for azinphos-methyl, thus lowering the MDL from that of the general screen (2.5 ug/cm²) to a level much below the safe level of 1.6 ug/cm².

REFERENCES

1. Maddy, K.T.: Estimated Safe Levels of Foliar Pesticide Residues to Allow Unprotected Workers Reentry Into Treated Fields In California. California Department of Food and Agriculture, Worker Health and Safety Branch. HS-1280. 1985.
2. Maddy, K.T., D.D. Meinders, S. Margetich: A Survey of Pear Orchards in Yolo and Sacramento Counties for Dislodgeable Foliar Organophosphate Residues at Harvest in July 1985. California Department of Food and Agriculture, Worker Health and Safety Branch. HS-1345. 1985.
3. Maddy, K.T., Y. Brittain, D. Alcoser, S. Margetich: A Survey of Selected Crops in the Central Valley for Dislodgeable Pesticide Residues on Foliage at the Time of Harvest, Summer 1985. California Department of Food and Agriculture, Worker Health and Safety Branch. HS-1366. 1985.